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**FIRST, SECOND AND THIRD GENERATION
HIGH ENERGY MATERIALS FROM CUBANE**

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Summary: New generations of super-energetic materials are required for the SDI mission. Cubane is a very dense, exceptionally energetic hydrocarbon; its heat of formation, density, and strain energy are all extraordinarily high -- in combination unexceeded by any other stable hydrocarbon. This dense, energetic system has 8 identical methine C-H groups at which hydrogen may be replaced by energy-rich substituents. Such substitution can provide smoke-free propellant components of enormous power, far superior to present-day metalized propellants. For example, tetrakis(dinitramino)cubane admixed with 15% BAMO/NMMO should have an I_{sp} (into vacuum) 24 seconds greater than HAP with 15% HTPPB. Realizing even a fraction of this would lead to enormous payload enhancements.

This project was designed to discover methods to attach highly oxidized, energetic groups onto the cubane nucleus. Specifically we are interested in developing the chemistry required to place nitro groups, trinitromethyl groups, fluorodinitromethyl groups, high-energy amine salts (e.g., perchlorates, nitrates, nitronates), etc. onto the cubane nucleus. These are very special groups, ones not often dealt with in organic synthesis. As these groups are neither ordinary nor easy to work with, manipulating them onto a cubane nucleus requires not only a fundamental understanding of cubane chemistry, but also development of new methodology tailored to the tasks at hand.

The enormous strain energy in the cubane system (+161 kcal/mole) makes cubanes very different chemically from ordinary compounds. Thus, we developed innovative methodology, indeed a whole new chemistry, to prepare cubanes appropriate to SDI's goals. New reactions have been invented, special reagents have been developed, and novel methods for functional group transformations have been found to provide for systematic elaboration of the cubane system.

We have improved enormously on the synthesis of cubane-1,2,4,7-tetracarboxylic acid. This critically important intermediate is at the heart of most efforts to prepare cubanes tetrasubstituted with high energy groups. All syntheses of the tetraacid, new and old, depend on the formation of stabilized cubane anions, an outgrowth of the methodological developments mentioned above (patent applied for). Our earliest synthesis, proceeding through zincation of cubane amides, was many steps long and capable at best of producing only a few hundred milligrams of the tetraacid. Although an important sequence as it provided the first sample of the tetraacid, this synthesis could not be scaled-up into practical use. The second method, made possible by our discovery of reverse transmetalation methodology, provided the tetraacid in multigram quantities, but involves use of mercury salts and therein presents an insurmountable environmental obstacle to industrial production. We have taken the ideas and innovations of these previous synthetic efforts, improved upon them, modified the intermediates, and now have a new and viable synthesis permitting the preparation of tetraacid in large quantities in a few steps from commercially available diacid. This method, ortho-magnesiation, is environmentally satisfactory and can be employed for commercial production.

Besides this important improvement in logistics, we have improved upon the synthesis of cubane-1,2,4,7-tetraisocyanate, and the derived tetra *tert*-butylcarbamate and tetraamine tetrahydrochloride. Plans for the synthesis of cubane tetraamine perchlorate on significant scale and the actual evaluation as this compound as a propellant by way of C* tests have been

developed. We have developed new ways of oxidizing amines and amine hydrochlorides to nitro compounds and are applying them to tetraamino cubane derivatives.

We have improved on the synthesis of 1,2-ureocubane and 1,2:4,7-bisureocubane. We have prepared for the first time a (nitramino)cubane by the successful nitration of 1,2-ureocubane obtaining thereby the N,N'-dinitraminoureocubane.

A synthesis for cubane-1,4-diol has been developed, and the its remarkably stable ditosylate has been prepared and characterized. We have made cubane bis-triflate from hypervalent iodide intermediates; this is the most nucleofugal-substituted cubane yet made, and should open pathways to cubane perchlorates. Cubane-1,4-diol is a promising material for the preparation of high-energy propellant binders

Our work on the cubyl cation has led to new concepts concerning the stability of dinitramines in the cubane system. We now feel that these very high-energy compounds may possess an unexpected (but very desirable) stability. If so, it is recognized that these compounds will very probably form the basis for the best cubane propellants. Work has been started to develop methodology appropriate to their preparation and characterization.

We have developed a whole of set of syntheses for cubane- T_d -tetracarboxylic acid. Groups on adjacent cubane positions interact significantly with one another through the intervening, labile cubane carbon-carbon bond. However, at the tetrasubstitution level there is a unique pattern in which no group is immediately adjacent to another. Such 1,3,5,7-tetrasubstituted cubanes, the so-called T_d -cubanes, should prove particularly stable kinetically, but still possess the great strain energy of the parent. We prepared the first of them: the tetraacid, the tetraamine hydrochloride, and the tetranitro derivative. Differential scanning calorimetry of the latter showed that decomposition of this very energetic cubane does not occur until over 270 °C!

Our first successful preparation of the T_d -cubanes was long and hard. We have transformed this arduous synthesis into a practical one -- 26 steps have been reduced to 8!! We now have a reliable method which we can transfer to others. We are ready to prepare sufficient quantities of these cubane compounds in this series to test previous hypotheses that the tetrakis(dinitramino)cubane, tetraaminocubane perchlorate and related high-energy derivatives will prove to be valuable propellant components.

We have prepared the first samples of cubane pentacid and cubane hexacid.

Working in collaboration with investigators at Thiokol Corp. we have shown that N_2O_5 or trifluoroacetyl nitrate in cold methylene chloride provide adequately for the tetra-N-nitration of the tetrakis(methylcarbamate) of cubane-1,2,4,7-tetramine whose synthesis we accomplished earlier. (Previous attempts to effect the N-nitration using nitronium tetrafluoroborate or 100% nitric acid failed completely.) This product is the key to the long-sought and SDI-critical material tetrakis(dinitramino)cubane. Hydrolysis of the nitrated carbamate should lead to the tetrakis(nitramine). With this in hand we can proceed (provided further funding is provided) with experiments for the introduction of a second nitro group on each of the amine nitrogens.

In the course of our SDI/ONR-sponsored work on the cubane system, there has been a rich fall-out applicable to non-SDI/ONR problems. This has permitted us to introduce new methodology for the synthesis of the important, heat-stable polyimide resins; to prepare polycubanes designed to be liquid ferroelectric crystal switches, to open the possibility of using cubanes to approach stabilized polyacetylene semiconductors, and to start work on the evaluation of substituted cubanes as antiviral agents. We have prepared many new cubanes. Forty-one of these have been submitted to the National Cancer Institute for screening against AIDS and various malignant tumors. To date, 11 compounds have shown interesting activity, sufficient to merit additional testing.

Following upon the receipt of supplemental funding for the purpose, a high resolution, high-field, nuclear magnetic resonance spectrometer capable of multi-nuclear work was purchased. That instrument has played (and continues to play) a major, indeed critical role in our discoveries of novel and important cubane chemistry and in our development of a real understanding of N-nitramine and N,N-dinitramine chemistry.

Technical Reports: Publications (copies attached) have been submitted in lieu of technical reports. A list follows:

Reverse Transmetalation: A Strategy for Obtaining Certain Otherwise Difficultly Accessible Organometallics

J. Am. Chem. Soc., 1987, 109, 948, P. E. Eaton, G. T. Cunkle, G. Marchioro and R. M. Martin

Synthesis of Zinc, Cadmium, Tin and Silicon Derivatives of Cubane.

Tetrahedron Letters, 1987, 28, 1055, P. E. Eaton, H. Higuchi and R. Millikan

Synthesis of Cubane Based High Energy Materials

SPIE Vol. 872 Propulsion, 1988, 30, R. J. Schmitt and J. C. Bottaro, and P. E. Eaton

X-ray Structures of Cubylcubane and 2-tert-Butylcubylcubane: Short Cage-Cage Bonds

J. Am. Chem. Soc., 1988, 110, 7232, R. Gilardi, P. E. Eaton, and M. Maggini

Conversion of Isocyanates to Nitro Compounds with Dimethyldioxirane in Wet Acetone

J. Org. Chem., 1988, 53, 5353, P. E. Eaton, G. W. Wicks

Magnesium Amide Bases and Amido-Grignards. Part I: Ortho Magnesiation

J. Am. Chem. Soc., 1989, 111, 8016, P. E. Eaton, C. -H. Lee and Y. Xiong

Synthesis of Iodocubanes by Decarboxylative Iodination

Tetrahedron Letters 1989, 30, 6967, P. E. Eaton, J. Tsanaktsidis

The Reactions of 1,4-Dihalocubanes with Alkylolithiums. The Case for 1,4-Cubadiyl

J. Am. Chem. Soc. 1990, 112, 876, P. E. Eaton, J. Tsanaktsidis

The Mechanism of the Olefin-to-Carbene Rearrangement for 9-Phenyl-1(9)-homocubene

J. Org. Chem. 1990, 55, 1321, P. E. Eaton, A. J. White.

HBr Cleavage of Cubane-1,4-dicarboxylic Acid. Easy Entry into the Nortwistbendane(ene) System

J. Org. Chem. 1990, 55, 2823, P. E. Eaton, R. Millikan

An Improved Preparation of 9-Oxabicyclo[3.3.1]nona-2,6-diene

Synthesis 1990, 483, P. E. Eaton, R. Millikan

Cubyl Cation

J. Am. Chem. Soc. 1990, 112, 3225, P. E. Eaton, C.-X. Yang and Y. Xiong

Automerization of Homocubylidene: Proof of a Reversible Olefin/Carbene Rearrangement

J. Am. Chem. Soc. 1990, 112, 4055, P. E. Eaton, R. B. Appell

Isomerization of the Cubane Radical Cation to Bridged 1,4-Bishomobenzene (Bicyclo[3.4.0]octa-2,6-diene-4,8-diyl) Radical Cation

J. Am. Chem. Soc. 1990, 112, 4567 X.-Z. Qin, A. D. Trifunac, P. E. Eaton, and Y. Xiong

Bond Lengths and Quadratic Force Field for Cubane

J. Am. Chem. Soc. 1991, 113, 1514 L. Hedberg, H. Hedberg, P. E. Eaton, N. Nodari and A. G. Robiette

Regiospecific Oxidation of Binor S and a New Pentacyclotetradecane System

J. Org. Chem. 1990, 55, 6105, P. E. Eaton, K. Pramod

Cubanourea. The First Fused-ring Cubane

J. Org. Chem. 1990, 55, 5746 P. E. Eaton, K. Pramod

Cubane Radical Cation in Liquid Hydrocarbons: Time-resolved Fluorescence Detected Magnetic Resonance Study

J. Am. Chem. Soc. 1991, 113, 670 X.-Z. Qin, A. D. Trifunac, P. E. Eaton, and Y. Xiong

Synthesis of AlkynylCyclooctatetraenes and Alkynylcubanes

J. Org. Chem. 1991, 56, 5138-5142 P. E. Eaton and D. Stössel

On the Discovery of Direct ortho-Magnesiation

J. Chinese Chem. Soc. (Taiwan) 1991 38, 303-306 P. E. Eaton, Y. Xiong and C.-H. Lee

The Preparation and Fate of Cubylcarbiny radicals

J. Am. Chem. Soc. 1991, 113, 7692-7697 P. E. Eaton, Y. C. Yip